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(54) Title: HERBICIDAL COMPOSITIONS CONTAINING TRIAZOLINONES (57) Abstract This invention relates to compositions comprising 1-aryl-4,5-dihydro-1,2,4-triazol-5(1H)-ones (triazolinones) in combination with the herbicide (2,4-dichlorophenoxy)acetic acid (2,4-D), or like substituted phenoxyalkanoic acids, or esters, or alkali metal or ammonium salts thereof; or with certain herbicidal sulfonylureas, or mixtures of these classes of compounds, to provide herbicidal compositions which are highly effective against a broad array of crop weeds, particularly broadleaf weeds, in crops such as wheat. <i>ncpr, ncpr, necoprop, isoproturon, dicamba</i>		

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HERBICIDAL COMPOSITIONS CONTAINING TRIAZOLINONES

This application is a continuation-in-part of application Serial No. 852,424, filed March 16, 1992, which in turn is a divisional of Serial No. 664,704, filed
5 March 5, 1991 (U.S. Patent 5,125,958), which in turn is a continuation-in-part of application Serial No. 462,360, filed December 28, 1989 (now abandoned), which in turn is a continuation-in-part of application Serial No. 383,109, filed July 20, 1989 (now abandoned), which
10 in turn is a continuation-in-part of application Serial No. 238,804, filed August 31, 1988 (now abandoned).

This invention relates to compositions comprising 1-aryl-4,5-dihydro-1,2,4-triazol-5(1H)-ones (hereinafter "triazolinones") in combination with other herbicidal
15 compounds, which compositions are useful as herbicides, especially against broadleaf weeds such as mustards, kochia, and the like. More particularly, it relates to these triazolinones in combination with the herbicide (2,4-dichlorophenoxy)acetic acid ("2,4-D"), or like
20 substituted phenoxyalkanoic acids, or herbicidally effective commercially available esters, or alkali metal or ammonium salts thereof; or with certain herbicidal sulfonylureas, as defined below (hereinafter "sulfonylureas"), or mixtures of these classes of
25 compounds, to provide post-emergence herbicidal compositions which are highly effective against a broad array of weeds which infest crops.

The triazolinones employed in this invention, their preparation, and their use in combination with other
30 herbicides including known herbicidal acetamides, benzothiodiazinones, triazines, dinitroanilines, and aryl ureas, is known from PCT International Application WO 90/02120, published March 9, 1990, discussed in further detail below, and whose U.S. counterpart is a
35 parent of the present continuation-in-part application. The combination of these triazolinones with 2,4-D, or

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other substituted phenoxy alkanoic acids, or with sulfonylureas is, however, not taught or suggested by this PCT publication.

5 In accordance with the present invention there are provided compositions comprising triazolinones, as defined herein, in combination with 2,4-D, or like herbicidally effective substituted phenoxy alkanoic acids, or with sulfonylureas, or mixtures of the latter compounds, in agriculturally acceptable carriers, which
10 are highly effective post-emergence herbicides in the control of a wide number of weeds which infest crops, particularly members of the mustard family, including shepherdspurse, bitter cress, blue mustard, tansymustard, flixweed, and field pennycress.

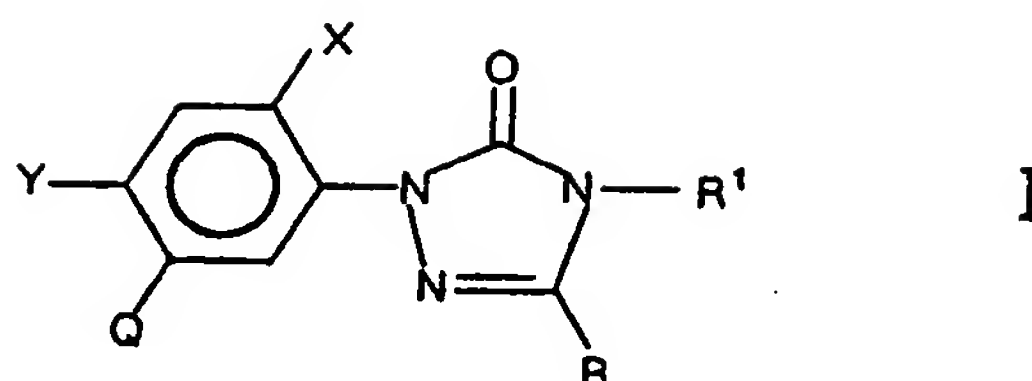
15 These compositions are particularly advantageous in that they provide for rapid kill of the majority of plant tissues, protection against the regrowth of the weeds and herbicidal control over a broad spectrum of broadleaf weeds, thus providing overall better
20 herbicidal control. These compositions are generally faster acting or more effective than any one component alone. In the case of 2,4-D, the combination allows the use of lower rate of 2,4-D, compared with a higher application rate of 2,4-D alone.

25 As described in PCT application WO 90/02120 (supra), the triazolinones employed as components of the claimed compositions comprise herbicidal 1-aryl-4,5-dihydro-1,2,4-triazol-5(1H)-ones of the formula

30

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in which

R is halogen or lower alkyl;

R¹ is haloalkyl;

X is hydrogen, halogen, alkyl, haloalkyl, alkoxy or
5 nitro;

Y is hydrogen, halogen, alkyl, alkoxy, haloalkyl,
halo lower alkylsulfinyl, or halo lower alkoxy;

Q is -CH(R²)C(R³)(R⁴)Q' or -CH=C(R⁴)Q';

R² is H or halogen;

10 R³ is halogen;

R⁴ is H or lower alkyl;

Q' is CO₂H, CO₂R⁵, CON(R⁶)(R⁷), CN, CHO, or C(O)R⁵;

R⁵ is alkyl, alkoxycarbonylalkyl, cycloalkyl,
benzyl, chlorobenzyl, alkylbenzyl, or haloalkylbenzyl;
15 and each of R⁶ and R⁷ is independently H, or a radical
which is an alkyl, cycloalkyl, alkenyl, alkynyl, alkoxy,
phenyl, benzyl, or SO₂R⁶ (in which R⁶ is other than H)
or is one of said radicals substituted by halogen,
alkyl, or cyano;

20 or a base-addition salt of the compound in which Q'
is CO₂H; or resolved isomers thereof; with the proviso
that any alkyl, alkenyl, or alkynyl moiety have less
than 6 carbon atoms and that any cycloalkyl moiety have
3 to 7 carbon atoms.

25 Preferred amongst these compounds where R², R³ and
R⁴ have the meanings set forth above, and R, R', X and Y
may be as follows: each of R and R¹ may, independently,
be lower alkyl (preferably methyl) or halo lower alkyl
such as fluoro lower alkyl (e.g. CF₂CHF₂ or CHF₂). R
30 may also be a halogen atom such as chlorine. Preferably

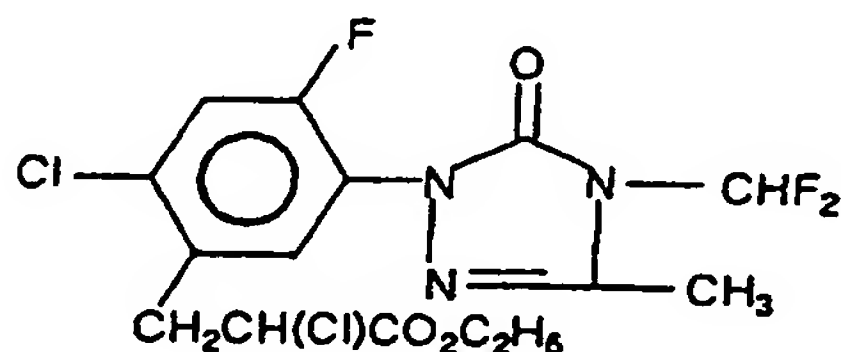
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R is methyl and R¹ is CHF₂. The substituent X may be hydrogen; halogen such as chlorine, bromine, or fluorine (preferably fluorine); alkyl such as lower alkyl (e.g. methyl); haloalkyl such as halo lower alkyl (e.g. CF₃, CH₂F or CHF₂); alkoxy such as lower alkoxy (e.g. methoxy); or nitro; and Y may be hydrogen; halogen such as chlorine, bromine, or fluorine (preferably bromine or chlorine); alkyl such as lower alkyl (e.g. methyl); alkoxy such as lower alkoxy (e.g. methoxy); haloalkyl such as halo lower alkyl (e.g. fluoroalkyl); halo lower alkylsulfinyl (e.g. -SOCHF₂); or halo lower alkoxy (e.g. -OCHF₂). Particularly preferred X, Y substituents are: 2-F, 4-Cl; 2-F, 4-Br; 2,4-diCl; 2-Br, 4-Cl; and 2-F, 4-CF₃.

It is preferable that any alkyl, alkenyl, alkynyl or alkylene moiety (such as the hydrocarbon moiety of an alkoxy or haloalkoxy group) have less than 6 carbon atoms, e.g. 1 to 3 or 4 carbon atoms, and that any cycloalkyl moiety have 3 to 7 ring carbon atoms, preferably 3-6 carbon atoms.

Any acidic compounds, including sulfonamides in which NR⁶R⁷ is NHSO₂R⁶, may be converted to the corresponding base addition salt by known methods.

Of particular interest in this invention are such compounds as ethyl 2-chloro-3-[2-chloro-4-fluoro-5-(4-difluoromethyl-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl)phenyl]propionate, (hereinafter "Compound P") having the formula



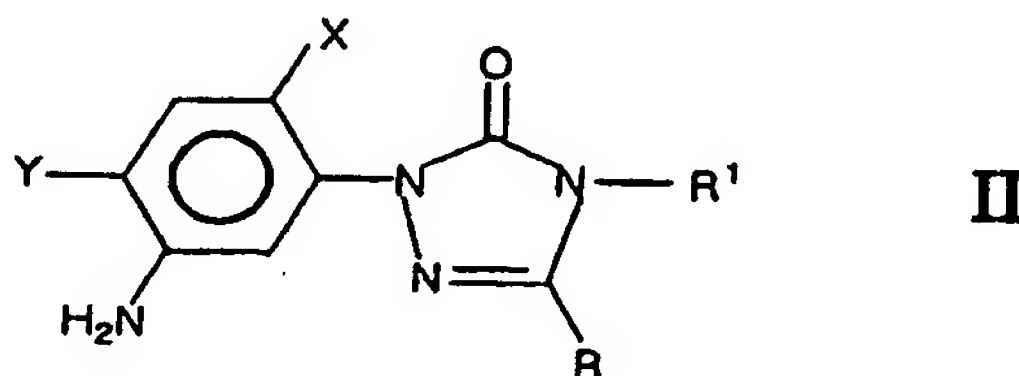
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and, e.g., the 4-chloro analog of this 4-fluoro compound.

Certain of the 1-aryl-4,5-dihydro-1,2,4-triazol-5(1H)-ones of the present invention contain an asymmetric carbon atom; the invention thus includes individual stereoisomers as well as racemic and non-racemic mixtures of enantiomers of the instant compounds. For example, ethyl 2-chloro-3-[2-chloro-4-fluoro-5-(4-difluoromethyl-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl)phenyl]propionate ("Compound P") is composed of a 2S and a 2R isomer. The 2S and 2R isomers of Compound P were separated by High Pressure Liquid Chromatography (HPLC), a method known to one skilled in the art, using a DIACEL CHIRALCEL OD column (distributed by Diacel Chemical Industries Ltd., Exton, Pa.), 4.6 mm ID x 250 mm, packed with silica gel of 10 μ m in particle size. Elution was accomplished with 1.5% ethanol in hexane at a flow rate of 1 mL/minute.

The triazolinone compounds may be prepared by methods described in PCT Application WO/02120 or in the following illustrative example, or by methods analogous and similar thereto which are within the skill of the art.

For instance, in Step A of the example below an amino compound of the formula (II)



(such as the compound shown in Example 1 of International patent publication WO 87/03782, published Jul. 2, 1987) is reacted (according to the Meerwein arylation reaction described below or a modification

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thereof) with an olefinic compound having the formula $\text{CHR}^2=\text{CR}^4\text{Q}'$ to form a compound of Formula I above in which Q is $-\text{CH}(\text{R}^2)\text{C}(\text{R}^3)(\text{R}^4)\text{Q}'$ and in which R^3 is halogen. In this type of reaction the amino compound is converted to a diazonium salt which then reacts with the olefinic compound through a radical mechanism. The Meerwein arylation reaction is discussed in an article by Doyle et al in J. Org. Chem., 42, 2431 (1977) which also describes a modification of that reaction in which an alkyl nitrite and a copper (II) halide are employed. (Step A of the example below employs the Doyle et al modification.) Instead, one may employ the unmodified reaction, in which the arenediazonium halide is initially prepared in an aqueous halogen acid solution and then mixed with the olefinic compound in the presence of an appropriate solvent (e.g. acetone) followed by the copper salt, such as copper (I) chloride.

Examples of olefinic compounds having the formula $\text{CHR}^2=\text{CR}^4\text{Q}'$ are methyl acrylate, ethyl acrylate, methyl methacrylate, methyl crotonate, methyl 3-chloroacrylate, methacrolein, vinyl methyl ketone, methacrylonitrile and acrylamide.

The product made by the reactions described above, i.e. a compound of Formula I in which Q is $-\text{CH}(\text{R}^2)\text{C}(\text{R}^3)(\text{R}^4)\text{Q}'$ and in which R^3 is halogen, may be treated to form other compounds of this invention. Dehydrohalogenation of that compound (e.g. with sodium hydride or other suitable base), when R^2 is H, yields a compound in which Q is $-\text{CH}=\text{C}(\text{R}^4)\text{Q}'$ (as in Step B of the example). That compound may be hydrogenated or halogenated to form a compound in which Q is $-\text{CH}(\text{R}^2)\text{C}(\text{R}^3)(\text{R}^4)\text{Q}'$ and R^3 is H (from hydrogenation, as in Step C) or R^2 and R^3 are halogen. When Q' is $-\text{CO}_2\text{H}$, the acidic compound of formula I may be converted to the

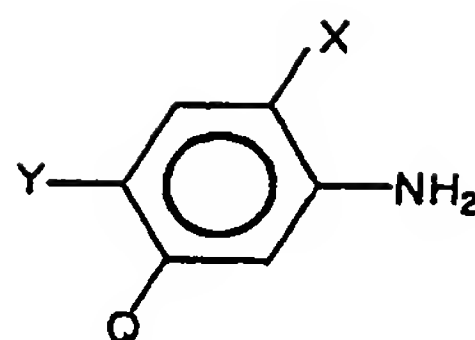
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corresponding amide, as by first treating with a reagent such as thionyl chloride to form the acid halide (wherein Q' is, for example, -COCl) and then reacting with ammonia or an amine. Alternative methods of amide formation, involving carbodiimide-mediated coupling, are known, as for example where the amide is formed from the carboxylic acid (of e.g. formula I) and the amine, in the presence of dicyclohexylcarbodiimide, 1-hydroxybenzotriazole and a base such as a tertiary amine, e.g. N,N-diisopropylethylamine or triethylamine, in a solvent such as tetrahydrofuran.

Instead of starting with an amino compound one may start with an otherwise identical compound having a CHO group in place of the NH₂ group and react it with a Wittig reagent (which may be a standard type of Wittig reagent or a modified type such as a Wadsworth-Emmons reagent). Thus, the reagent may be an alkylidene phosphorane whose alkylidene group has the formula =C(R⁴)Q' such as (C₆H₅)₃P=CHCO₂R⁵ or it may be a phosphonate ylide comprising a phosphonate diester in which the group directly attached to the P atom has the formula -CH(R⁴)Q' such as (C₂H₅O)₂P(O)CH₂CO₂R⁵, used together with, say, NaH in known manner. R⁵ is preferably lower alkyl such as methyl or ethyl. The product thereof may be hydrogenated to produce a compound of Formula I in which R² and R³ are each hydrogen, or it may be halogenated (e.g. with chlorine) to form a compound of Formula I in which R² and R³ are each halogen. The latter compound may in turn be dehydrohalogenated to form a compound in which R⁴ is halogen and then hydrogenated to form a compound of Formula I in which R⁴ is halogen and R³ and R² are H.

Instead of starting with a compound containing the triazolinone ring and adding thereto the Q substituent, one may start with a compound of the formula

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III

and then form the triazolinone ring. Compounds of Formula III are shown, for instance, in published European patent applications 300387 and 300398. The NH₂ group may be converted to a triazolinone ring in known manner. For instance it may be converted to an NHNH₂ (i.e. hydrazine) group in the conventional fashion, by diazotization followed by reduction with sodium sulfite, and the hydrazine group may be converted to a triazolinone ring.

When X and Y are substituents other than H, such substituents may be introduced at various stages of the process, e.g., prior to the formation of a compound containing the Q substituent. One or both of these substituents may be introduced after the introduction of the Q substituent; for instance, a chlorine substituent on the benzene ring may be introduced during one of the halogenation steps which modify the Q substituent, as described above.

The preparation of the triazolinone components is illustrated by the following example. In this application, all parts are by weight and all temperatures are in °C unless otherwise indicated.

EXAMPLE

METHYL 3-[2,4-DICHLORO-5-(4-DIFLUOROMETHYL-4,5-DIHYDRO
3-METHYL-5-OXO-1H-1,2,4-TRIAZOL-1-YL) PHENYL] PROPIONATE

Step A Methyl 2-Chloro-3-[2,4-dichloro-5-(4-difluoro-
methyl-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-
triazol-1-yl)phenyl]propionate

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To a cold (0°C), stirred mixture of 28.7 g (0.333 mole) of methyl acrylate, 2.51 g (0.0244 mole) of tert-butyl nitrite, and 2.6 g (0.019 mole) of copper (II) chloride in 50 mL of acetonitrile was added dropwise a solution of 5.0 g (0.016 mole) of 1-(5-amino-2,4-dichlorophenyl)-4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-one in 15 mL of acetonitrile. After complete addition the reaction mixture was allowed to warm to room temperature and was stirred for approximately 18 hours. The reaction mixture was diluted with 15 mL of 2N hydrochloric acid solution. The mixture was extracted with four portions of diethyl ether. The combined extracts were dried over anhydrous magnesium sulfate, filtered, and the filtrate evaporated under reduced pressure to give an oil. The oil was purified by column chromatography on silica gel, eluting with n-heptane:ethyl acetate (4:1) to give 5.0 g of methyl 2-chloro-3-[2,4-dichloro-5-(4-difluoromethyl-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl)phenyl]propionate as an oil.

Step B Methyl 3-[2,4-dichloro-5-(4-difluoromethyl-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl)phenyl]-2-propenoate

To a stirred, cold (0°C) solution of 4.16 g (0.0100 mole) of methyl 2-chloro-3-[2,4-dichloro-5-(4-difluoromethyl-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl)phenyl]propionate in 15 mL of N,N-dimethylformamide was added portionwise 0.29 g (0.012 mole) of sodium hydride. After complete addition the reaction mixture was allowed to warm to room temperature and was stirred for 30 minutes. The reaction mixture was heated at 60°C for six hours, then was stirred at room temperature for approximately 18 hours. The reaction mixture was poured into ice water, and the resultant

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aqueous mixture was extracted with four portions of diethyl ether. The extracts were combined and washed successively with water and an aqueous, saturated sodium chloride solution. The washed organic phase was dried
5 over anhydrous magnesium sulfate and was filtered. The filtrate was evaporated under reduced pressure to give a white foam. The foam was purified by column chromatography on silica gel, eluting with n-heptane:ethyl acetate (4:1), to give 1.63 g of methyl 3-
10 [2,4-dichloro-5-(4-difluoromethyl-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl)phenyl]-2-propenoate as a solid, m.p. 148-151°C.

Step C Methyl 3-[2,4-dichloro-5-(4-difluoromethyl-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-
15 1-yl)phenyl]propionate

Hydrogenation of 0.59 g (0.0016 mole) of methyl 3-[2,4-dichloro-5-(4-difluoromethyl-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl)phenyl]-2-propenoate over
20 approximately 0.2 g (0.0009 mole) of platinum (IV) oxide in approximately 15 mL of ethyl acetate gave 0.59 g of methyl 3-[2,4-dichloro-5-(4-difluoromethyl-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl)phenyl]propionate as a clear oil, which crystallized upon standing. The
25 crystals were triturated with petroleum ether and recovered by filtration, m.p. 70-73°C.

The preferred triazolinone component of the compositions of this invention as stated above, namely ethyl 2-chloro-3-[2-chloro-4-fluoro-5-(4-difluoromethyl-4,5-dihydro-3-methyl-5-oxo-(1H)-1,2,4-triazol-1-
30 yl)phenyl]propionate, (i.e., "Compound P") may readily be prepared in accordance with the procedures of the foregoing example, but substituting 1-(5-amino-4-chloro-2-fluorophenyl)-4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-one and ethyl acrylate for 1-(5-

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amino-2,4-dichlorophenyl)-4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-one and methyl acrylate in Step A.

As stated above, the second component of the herbicidal triazolinone composition of this invention is preferably a chlorinated phenoxy lower alkanolic acid compound, and most particularly (2,4-dichlorophenoxy)-acetic acid, commonly known as 2,4-D, and the esters, or alkali metal or ammonium salts thereof, all of which are available commercially from several sources, e.g. Chevron (Weed-B-Gon™), Pennwalt (Pennamine™D), and the like. However, there may also be employed related, commercially available herbicidal chlorinated lower alkylphenoxy alkanolic acid compounds as 4-(4-chloro-2-methylphenoxy)acetic acid, commonly known as MCPA; (4-chloro-2-methylphenoxy)butanoic acid, commonly known as MCPB; 2-(4-chloro-2-methylphenoxy)propionic acid, commonly known as MCPP or mecoprop, and its herbicidally active isomers; and the esters, salts, and amines of each of the above, such as MCPA amine, or MCPA ester, (Riverdale Chemical Co., Glenwood, Illinois), MCPP-p (BASF), or the like.

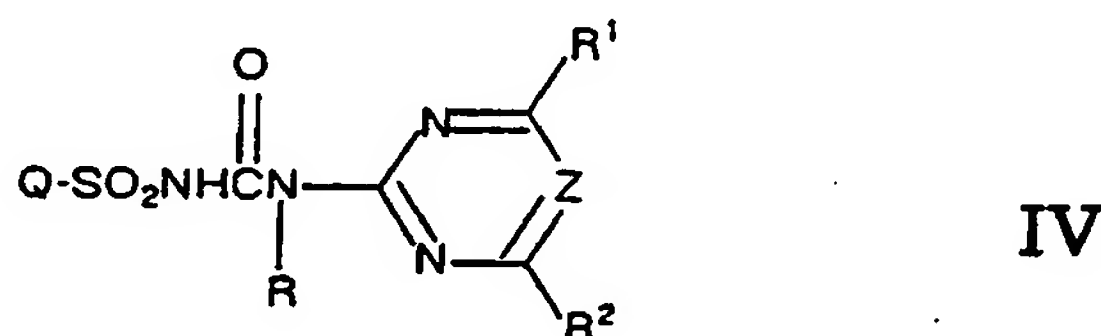
By the term esters, as used above to define 2,4-D and related phenoxy alkanolic acid derivatives, is meant principally those prepared from C₁-C₁₀ aliphatic alcohols. Of these, the isooctyl ester of 2,4-D, which is commercially available as Weedtime II™ ("2,4-D ester") from Applied Biochemists Inc. (Mequon, WI), is preferred. The corresponding salts are generally alkali metal or ammonium salts, commercially available as, e.g., the potassium salt, or as the ammonium salt, (commonly referred to as "amines" of 2,4-D compounds), e.g., the dimethylamine salt. (See, e.g., Farm

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Chemicals Handbook, Meister Publishing Co. (1990), pp. C-87-88.). The compound MCPP-p, set forth above, is the resolved (+) isomer of the above-defined commercially available mecoprop. (See Farm Chemicals Handbook, 5 supra, pp. C-183-185.).

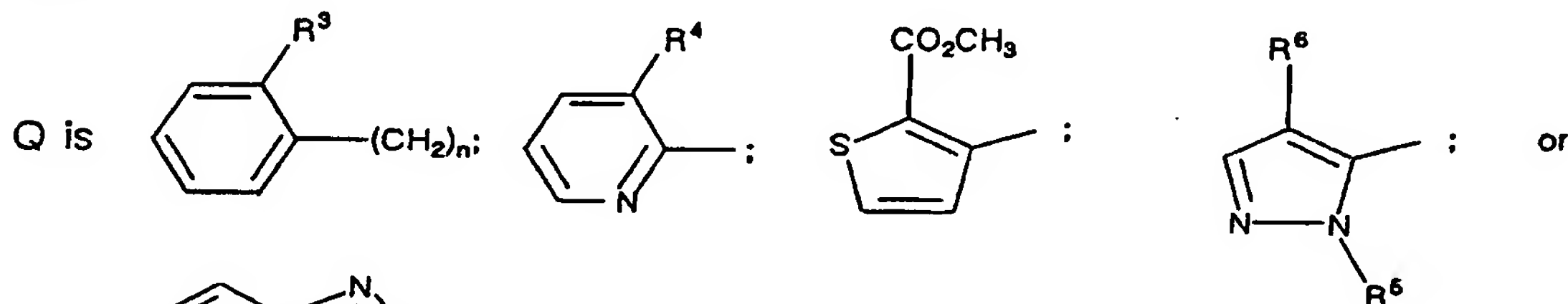
Alternatively, in a further embodiment of this invention, the triazolinones may instead be combined with herbicidal sulfonylureas of the formula

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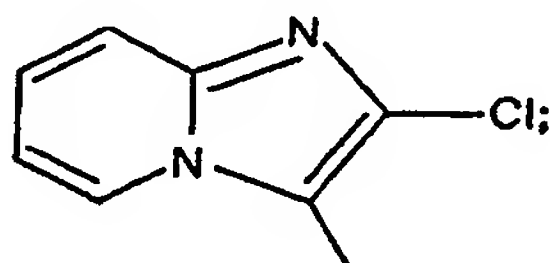


wherein

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20



Z is N or CH;

R is H or -CH₃;

R¹ and R² are -OCH₃ or -CH₃;

25

R³ is CO₂CH₃ or Cl;

n is 0 or 1;

R⁴ is CN(CH₃)₂ or SO₂C₂H₅;

30

R⁵ is CH₃ or ; and

R⁶ is CR⁷, wherein R⁷ is -OCH₃ or -OC₂H₅.

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Included amongst the sulfonylureas which, in accordance with this invention, may be used in combination with the herbicidal triazolinones are known commercially available herbicides such as:

- 5 methyl 2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]benzoate (metsulfuron-methyl), (ALLY™ - E.I. DuPont, Wilmington, Del.);
- 2-chloro-N-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide (chlorsulfuron),
- 10 (GLEAN™ - E.I. DuPont, Wilmington, Del.);
- methyl 2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]methyl]benzoate (bensulfuron-methyl), (LONDAX™ - E.I. DuPont, Wilmington, Del.);
- methyl 2-[[[[(N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino]sulfonyl]benzoate
- 15 (tribenuron-methyl), (EXPRESS™ - E.I. DuPont, Wilmington, Del.);
- methyl 3-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylate
- 20 (thifensulfuron-methyl), (HARMONY™ - E.I. DuPont, Wilmington, Del.);
- ethyl 5-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-1-methyl-1H-pyrazole-4-carboxylate (pyrazosulfuron-ethyl), (SIRIUS™ - Nissan
- 25 Chemical Industries, Ltd., Tokyo, Japan);
- 2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-N,N-dimethyl-3-pyridinecarboxamide (nicosulfuron), (ACCENT™ - E.I. DuPont, Wilmington, Del.);
- 30 methyl 5-[[[[(4,6-dimethyl-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-1-(2-pyridinyl)-1H-pyrazole-4-carboxylate (NC-330, - available from Nissan Chemical Industries, Ltd., Tokyo, Japan);
- 3-ethylsulfonyl-N-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-2-pyridinylsulfonamide (DPXE 9636, -
- 35 available from E.I. DuPont Co., Wilmington, Del.); and

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N-[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-2-chloroimidazo-[1,2-a]pyridinecarboxamide (TH-913, - available from Takeda Chemical Industries, Ltd., Tokyo, Japan).

5 The active herbicidal compositions of this invention may also be used in combination with other herbicides, e.g. they may be mixed with, say, an equal or larger amount of known herbicides such as N-(1-ethylpropyl)-
10 2,4-dinitro-3,4-xylidene (pendamethalin); (RS)-2-[2,4-dichlorophenoxy]phenoxy]propionic acid (diclofop); 2,4-difluoro-2-(α,α,α -trifluoro-m-tolyloxy)nicotinalanilide (diflufenican); (\pm)-2-[4-(6-chloro-1,3-benzoxazol-2-yloxy)phenoxy]propionic acid (fenoxaprop); 3-p-cumenyl-
15 1,1-dimethylurea (isoproturon); 4-hydroxy-3,5-diiodobenzonitrile (ioxynil); or 3,6-dichloro-o-anisic acid (dicamba).

 The weight ratio of triazolinone to 2,4-D, or to the sulfonylurea in order to obtain the desired herbicidal effect is not critical, and may be varied widely. Thus,
20 for example, the ratio of triazolinone to 2,4-D may range from about 1:125 to 1:2, more preferably 1:17 to 1:4, while the ratio of triazolinone to sulfonylurea may range from about 8:1 to 30:1, more preferably 1:1 to 16:1. It will be understood that these ranges may be
25 adjusted by those skilled in the art depending upon the crops involved, field conditions and the like.

FORMULATIONS

 For herbicidal application, the active compositions
30 are formulated by admixture in herbicidally effective amounts with adjuvants and carriers normally employed in the art for facilitating the dispersion of active ingredients for the particular utility desired, recognizing the fact that the formulation and mode of
35 application of a toxicant may affect the activity of the material in a given application. Thus, for agricultural

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use the present herbicidal compositions may be formulated as granules of relatively large particle size, as water-soluble or water-dispersible granules, as powdery dusts, as wettable powders, as emulsifiable concentrates, as solutions, or as any of several other known types of formulations, depending on the desired mode of application.

These herbicidal compositions may be applied either as water-diluted sprays, or dusts, or granules to the areas in which suppression of vegetation is desired. These formulations may contain as little as 0.1%, 0.2% or 0.5% to as much as 95% or more by weight of active ingredients.

Dusts are free flowing admixtures of the active ingredient with finely divided solids such as talc, natural clays, kieselguhr, flours such as walnut shell and cottonseed flours, and other organic and inorganic solids which act as dispersants and carriers for the toxicant; these finely divided solids have an average particle size of less than about 50 microns. A typical dust formulation useful herein is one containing 1.0 part or less of the herbicidal composition and 99.0 parts of talc.

Wettable powders, also useful formulations for both pre- and postemergence herbicides, are in the form of finely divided particles which disperse readily in water or other dispersant. The wettable powder is ultimately applied to the soil either as a dry dust or as an emulsion in water or other liquid. Typical carriers for wettable powders include Fuller's earth, kaolin clays, silicas, and other highly absorbent, readily wet inorganic diluents. Wettable powders normally are prepared to contain about 5-80% of active ingredient, depending on the absorbency of the carrier, and usually also contain a small amount of a wetting, dispersing or emulsifying agent to facilitate dispersion. For

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example, a useful wettable powder formulation contains 80.8 parts of the herbicidal compound, 17.9 parts of Palmetto clay, and 1.0 part of sodium lignosulfonate and 0.3 part of sulfonated aliphatic polyester as wetting agents. Other wettable powder formulations are:

<u>Component:</u>		<u>% by Wt.</u>
	Active ingredients	40.00
	Sodium lignosulfonate	20.00
10	Attapulgite clay	<u>40.00</u>
	Total	100.00
<u>Component:</u>		<u>% by Wt.</u>
	Active ingredients	90.00
15	Diethyl sodium sulfosuccinate	0.10
	Synthetic fine silica	<u>9.90</u>
	Total	100.00
<u>Component:</u>		<u>% by Wt.</u>
20	Active ingredients	20.00
	Sodium alkylnaphthalenesulfonate	4.00
	Sodium lignosulfonate	4.00
	Low viscosity methyl cellulose	3.00
	Attapulgite clay	<u>69.00</u>
25	Total	100.00
<u>Component:</u>		<u>% by Wt.</u>
	Active ingredients	25.00
	Base:	75.00
30	96% hydrated aluminum magnesium silicate	
	2% powdered sodium lignosulfonate	
	2% powdered anionic sodium alkyl-naphthalenesulfonate	
	Total	<u>100.00</u>
35		

Frequently, additional wetting agent and/or oil will be

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added to the tank-mix for postemergence application to facilitate dispersion on the foliage and absorption by the plant.

Other useful formulations for herbicidal applications are emulsifiable concentrates (ECs) which are homogeneous liquid or paste compositions dispersible in water or other dispersant, and may consist entirely of the herbicidal compound and a liquid or solid emulsifying agent, or may also contain a liquid carrier, such as xylene, heavy aromatic naphthas, isophorone, or other non-volatile organic solvent. For herbicidal application these concentrates are dispersed in water or other liquid carrier, and normally applied as a spray to the area to be treated. The percentage by weight of the essential active ingredients may vary according to the manner in which the composition is to be applied, but in general comprise 0.5 to 95% of active ingredient by weight of the herbicidal composition.

The following are specific examples of emulsifiable concentrate formulations:

<u>Component:</u>	<u>% by Wt.</u>
Active ingredients	53.01
25 Blend of alkylnaphthalenesulfonate and polyoxyethylene ethers	6.00
Epoxidized soybean oil	1.00
Xylene	<u>39.99</u>
Total	100.00
30	
<u>Component:</u>	<u>% by Wt.</u>
Active ingredients	10.00
Blend of alkylnaphthalenesulfonate and polyoxyethylene ethers	4.00
35 Xylene	<u>86.00</u>
Total	100.00

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Flowable formulations are similar to ECs except that the active ingredient is suspended in a liquid carrier, generally water. Flowables, like ECs, may include a small amount of a surfactant, and contain
 5 active ingredient in the range of 0.5 to 95%, frequently from 10 to 50%, by weight of the composition. For application, flowables may be diluted in water or other liquid vehicle, and are normally applied as a spray to the area to be treated.

10 The following are specific examples of flowable formulations:

<u>Component:</u>		<u>% by Wt.</u>
	Active ingredients	46.00
15	Colloidal magnesium aluminum silicate	0.40
	Sodium alkyl naphthalenesulfonate	2.00
	Paraformaldehyde	0.10
	Water	40.70
	Propylene glycol	7.50
20	Acetylenic alcohols	2.50
	Xanthan gum	<u>0.80</u>
	Total	100.00
<u>Component:</u>		<u>% by Wt.</u>
25	Active ingredients	45.00
	Water	48.50
	Purified smectite clay	2.00
	Xanthan gum	0.50
	Sodium alkyl naphthalenesulfonate	1.00
30	Acetylenic alcohols	<u>3.00</u>
	Total	100.00

Typical wetting, dispersing or emulsifying agents used in agricultural formulations include, but are not
 35 limited to, the alkyl and alkylaryl sulfonates and sulfates and their sodium salts; alkylaryl polyether alco-

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hols; sulfated higher alcohols; polyethylene oxides; sulfonated animal and vegetable oils; sulfonated petroleum oils; fatty acid esters of polyhydric alcohols and the ethylene oxide addition products of such esters; and the addition product of long-chain mercaptans and ethylene oxide. Many other types of useful surface-active agents are available in commerce. The surface-active agent, when used, normally comprises from 1 to 15% by weight of the composition.

Other useful formulations include simple solutions or suspensions of the active ingredient in a relatively non-volatile solvent such as water, corn oil, kerosene, propylene glycol, or other suitable solvents. The following illustrate specific suspensions:

15

Oil Suspension:% by Wt.

Active ingredients	25.00
Polyoxyethylene sorbitol hexaoleate	5.00
Highly aliphatic hydrocarbon oil	<u>70.00</u>
20 Total	100.00

Aqueous Suspension:% by Wt.

Active ingredients	40.00
Polyacrylic acid thickener	0.30
25 Dodecylphenol polyethylene glycol ether	0.50
Disodium phosphate	1.00
Monosodium phosphate	0.50
Polyvinyl alcohol	1.00
Water	<u>56.70</u>
30 Total	100.00

Other useful formulations for herbicidal applications include simple solutions of the active ingredient in a solvent in which it is completely soluble at the desired concentration, such as acetone, alkylated naphthalenes, xylene, or other organic solvents. Granular

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formulations, wherein the toxicant is carried on relatively coarse particles, are of particular utility for aerial distribution or for penetration of cover crop canopy. Pressurized sprays, typically aerosols wherein the active ingredient is dispersed in finely divided form as a result of vaporization of a low boiling dispersant solvent carrier, such as the Freon fluorinated hydrocarbons, may also be used. Water-soluble or water-dispersible granules are also useful formulations for herbicidal application of the present compounds. Such granular formulations are free-flowing, non-dusty, and readily water-soluble or water-miscible. The soluble or dispersible granular formulations described in U.S. Patent No. 3,920,442 are useful herein with the present herbicidal compounds. In use by the farmer on the field, the granular formulations, emulsifiable concentrates, flowable concentrates, solutions, etc., may be diluted with water to give a concentration of active ingredient in the range of say 0.1% or 0.2% to 1.5% or 2%.

The active herbicidal compositions of this invention may be formulated and/or applied with insecticides, fungicides, nematocides, plant growth regulators, fertilizers, or other agricultural chemicals and may be used as effective soil sterilants as well as selective herbicides in agriculture. In applying an active composition of this invention, whether formulated alone or with other agricultural chemicals, an effective amount and concentration of the active compounds are of course employed; for example, amounts as low as 1 g/ha or less, e.g. 1-125 g/ha, may be employed for control of broadleafed weeds with little or no injury to crops such as maize or wheat. For field use, where there are losses of herbicide, higher application rates (e.g. four times the rates mentioned above) may be employed.

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Herbicidal Activity

5 The test species used in demonstrating the herbicidal postemergence activity of the compositions of this invention are set forth in each of the tables below. These tests were conducted on populations of these species located in fields at various locations in the United States, the United Kingdom or France. The crops were planted; the weeds were either planted or grew naturally at these locations.

10 Test plots were typically 10.0 ft by 20.0 ft, with 6.7 ft by 20.0 ft treated with a given rate of a herbicide or herbicide combination. (At any given location these were at least three, and most always, four replications of the individual treatments.) Control of the
15 weed species and injury to the crop was assessed on a percent basis, relative to the nearest untreated area. Percent control was determined by a method similar to the 0 to 100 rating system disclosed in "Research
20 Methods in Weed Science," 2nd ed., B. Truelove, Ed.; Southern Weed Science Society; Auburn University, Auburn, Alabama, 1977. This rating system is set forth in the following table, captioned "Herbicide Rating System."

25 The herbicides were applied to the test area by spraying an aqueous solution or suspension or emulsion of the compound or combination of compounds over the entire designated area. The formulated herbicides were diluted to a concentration appropriate for the desired application rate on the basis of a spraying rate of 20
30 gallons per acre. Unless otherwise noted, no surfactant or other adjuvant was added to the spray solution.

For example, to treat the four test replicates at a single location with 0.031 lb/acre of Compound P, 1.04
35 ml of the 2 lb/gal emulsifiable concentrate formulation was mixed with 1500 ml of water. The solution was

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sprayed through T-Jet Flat Fan 8002E nozzles (T-Jet Spraying Systems") at 30 psi pressure.

Applications were typically made when the weed species were 1-3 inches tall. Percent control was
5 rated at various times after application, as shown in the tables below, using the following "Rating System."

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Herbicide Rating System

<u>Rating Percent Control</u>	<u>Description of Main Categories</u>	<u>Crop Description</u>	<u>Weed Description</u>
0	No effect	No crop reduction or injury	No weed control
10	Slight effect	Slight dis- coloration or stunting	Very poor weed control
20		Some dis- coloration, stunting or stand loss	Poor weed control
30		Crop injury more pronounced but not lasting	Poor to defi- cient weed control
40	Moderate effect	Moderate injury, crop usually recovers	Deficient weed control
50		Crop injury more lasting, recovery doubt- ful	Deficient to moderate weed control
60		Lasting crop injury, no recovery	Moderate weed control
70	Severe	Heavy injury and stand loss	Control some- what less than satisfactory
80		Crop nearly des- troyed, a few survivors	Satisfactory to good weed control
90		Only occasional live plants left	Very good to excellent control
100	Complete effect	Complete crop destruction	Complete weed destruction

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TABLES

Herbicidal data at selected application rates are given for various compounds of the invention in the tables below. The test compounds are identified in footnotes of the tables.

In Tables I-IX the triazolinone ethyl-2-chloro-3-[2-chloro-4-fluoro-5-(4-difluoromethyl-4,5-dihydro-3-methyl-5-oxo-(1H)-1,2,4-triazol-1-yl)phenyl]propionate (designated in the tables as "Compound P") was employed, but it will be understood that other triazolinones described above may be employed instead.

The other active ingredients of the claimed herbicidal compositions are as identified in the tables.

The scientific names of all the weed species used in these trials are presented in Table X.

In the tables, the tests were carried out using formulations in which Compound P was first admixed with varying amounts of surfactants and aromatic hydrocarbon solvents. These formulations were then applied to various test plants, and at various rates, as indicated in these tables, using the triazolinone Compound P in combination with the other herbicides of this invention, also indicated in these tables.

Examples of two such formulations of Compound P employed herein are as follows:

	<u>Components</u> (50 g/liter)	<u>wt/%</u>
30	Cmpd P (91.1% purity)	6.06
	Emulsifier 1 ^a	3.20
	Emulsifier 2 ^b	3.20
	Dispersant ^c	1.60
	Aromatic 100 (solvent) ^d	85.94

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First Formulation (2 lbs/gal)

	Cmpd P (95% purity)	26.97
	Emulsifier 1 ^a	1.95
5	Emulsifier 2 ^b	2.60
	Dispersant ^c	1.95
	Aromatic 100 ^d	66.53

Second Formulation (2 lbs/gal)

10	Cmpd P (91.4% purity)	24.42
	Emulsifier 1 ^a	3.50
	Emulsifier 2 ^b	1.40
	Dispersant ^c	2.10
15	Aromatic 200 ^e	68.58

20 a An emulsifier consisting of 64% of an anionic calcium salt of dodecylbenzene sulfonate, 16% of a nonionic 6-molar ethylene oxide condensation product of nonylphenol, and 20% butanol (Whitco Chemical Corp., Organics Div., New York, NY)

25 b An emulsifier consisting of 56% of an anionic calcium salt of dodecylbenzene sulfonate, 24% of a nonionic 30-molar ethylene oxide condensation product of nonylphenol, and 20% butanol (Whitco Chemical Corp., Organics Div., New York, NY)

30 c A dispersant consisting of a nonionic paste of 100% polyalkylene glycol ether (Union Carbide Chemical and Plastics Co. Inc., Danbury, CT)

35 d B.P. 156-167°C (Exxon Chemical Co., Houston, Texas)

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e B.P. 231-233°C (Exxon Chemical Co., Houston, Texas)

Of these latter two solvents, the second formulation, which was less phytotoxic, is preferred.

5

The formulations of the 2,4-D and sulfonylurea components described in the tables are all well-known to those skilled in the art, and are commercially available materials which may be routinely mixed with the above
10 Compound P formulations at desired ratios and dilutions, desirably with water, necessary to obtain the application rates specified in the tables.

It will be apparent that various modifications may be made in the formulations and applications of the
15 compositions of this invention without departing from the inventive concepts herein as defined in the claims.

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Table I

Weed Control by Compound P Alone and in Combination with Express^(a) and Harmony^(b) Herbicides Evaluated 23 Days after Treatment

<u>Weed Species</u> <u>Appl. Rate^(c)</u>	<u>Cpd. P</u>		<u>Express</u>						<u>Harmony</u>					
	<u>Alone</u>		<u>Alone</u>		<u>Comb.</u>				<u>Alone</u>		<u>Comb.</u>			
	L	H	L	H	LL	LH	HL	HH	L	H	LL	LH	HL	HH
<u>Percent Control</u>														
Redroot Pigweed	95	100	82	89	95	100	99	100	100	100	100	100	100	100
Giant Ragweed	30	55	56	65	54	68	58	63	83	86	84	88	83	91
Common	68	94	100	100	98	100	98	100	100	99	99	100	100	100
Lambsquarter														
Wild Sunflower	56	78	84	93	78	90	79	95	100	100	100	100	100	100
Kochia	64	83	98	100	78	99	96	96	90	93	93	100	97	99
Wild Buckwheat	48	61	64	50	41	80	68	80	92	96	95	100	97	99
Russian Thistle	66	87	100	100	94	100	88	98	100	100	99	100	99	99
Wild Mustard	24	31	99	98	81	99	89	99	75	86	74	84	80	84
Wild Garlic	54	69	73	83	78	88	74	86	96	94	88	94	90	93

Application Rate^(c)

<u>Compound</u>	<u>Low Rate (L)</u>	<u>High Rate (H)</u>
Compound P	0.008	0.015
Express	0.004	0.008
Harmony	0.008	0.015

L = Low rate

H = High Rate

LL = Low rate of Cpd. P + low rate of standard

LH = Low rate of Cpd. P + high rate of standard

HL = High rate of Cpd. P + low rate of standard

HH = High rate of Cpd P + high rate of standard

(a) Express: methyl 2-[[[N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino]sulfonyl]benzoate (tribenuronmethyl)
(DuPont, Wilmington, Del.)

(b) Harmony: methyl 3-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylate (thifensulfuronmethyl)
(DuPont, Wilmington, Del.)

(c) Rate of application is in pounds of active ingredient/acre (lb/a).

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Table II

Percent Weed Control by Compound P Alone and in Combination with Express®
Herbicide in Winter Barley and Winter Wheat Evaluated 22 Days After Treatment

<u>Weed Species</u>	<u>Cpd. P</u> <u>(7 g/ha)^(a)</u>	<u>Express</u> <u>(19 g/ha)</u>	<u>Cpd. P + Express</u> <u>(7 +19 g/ha)</u>
Catchweed Bedstraw	100	65	97
Red Deadnettle	93	97	100
Wild Chamomile	97	97	97
Field Forget-Me-Not	95	97	100
Corn Poppy	61	99	95
Common Chickweed	99	100	100
Ivyleaf Speedwell	92	92	97
Persian Speedwell	65	85	97
Field Violet	65	90	97

Table III

Percent Weed Control by Compound P Alone and in Combination with Ally®^(b)
Herbicide Evaluated 30 Days After Treatment

<u>Herbicide</u>	<u>Rate</u> <u>g/ha^(a)</u>	<u>Percent Control</u>						
		<u>Pineapple-</u> <u>weed</u>	<u>Field Violet</u>	<u>Mouseear-</u> <u>grass</u>	<u>Blackgrass</u>	<u>Common</u> <u>Chickweed</u>	<u>Ivyleaf</u> <u>Speedwell</u>	<u>Prostrate</u> <u>Knotweed</u>
Cpd. P	10	19	0	0	0	69	96	99
	15	25	10	0	0	71	99	99
	30	39	17	14	0	81	100	100
	60	56	36	25	0	86	100	100
Ally	3	34	0	0	0	81	7	95
Cpd. P + Ally	15+3	53	47	33	0	89	100	100

(a) Rate of application is in grams of active ingredient/hectare (g/ha).

(b) Ally: methy 2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]benzoate (metsulfuronmethyl)
(DuPont, Wilmington, Del.)

Table IV
Postemergence Wheat Tolerance (Percent Injury) of Compound P Alone and in Combination with Ally® Herbicide
7 Days After Treatment and Weed Control
30 Days After Treatment

Percent Control											
Herbicide	Rate g/ha(a)	PI(b) To Wheat	Catchweed Bedstraw	Field Violet	Persian Speedwell	Common Chickweed	Field- Forget- Me-Not	Cutleaf Cranesbill	Red Deadnettle	Ivyleaf Speedwell	
Cpd. P	7.5	1	78	13	10	10	13	30	8	15	
	15	4	89	11	12	6	7	10	13	69	
	30	8	96	45	12	9	5	10	8	89	
Ally	6	0	14	79	74	78	55	73	64	0	
Cpd. P + Ally	7.5 + 6	1	67	81	67	73	53	80	54	30	
	15 + 6	3	79	92	86	89	83	93	82	81	

(a) Rate of application is in grams of active ingredient/hectare (g/ha).

(b) PI is percent injury to wheat.

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Table V

Percent Control of Weeds and Tolerance of Wheat (Percent Injury) with
Compound P Alone and in Combination with Ally® Herbicide

<u>Herbicide</u>	<u>Rate</u> <u>g/ha^(a)</u>	<u>Percent</u> <u>Injury to</u> <u>Wheat</u>	<u>Percent Control</u>		
			<u>White</u> <u>Mustard</u>	<u>Persian</u> <u>Speedwell</u>	<u>Catchweed</u> <u>Bedstraw</u>
		<u>7 DAT^(b)</u>	<u>30 DAT</u>	<u>30 DAT</u>	<u>30 DAT</u>
Cpd. P	10	2	71	91	90
	15	4	90	95	92
	30	6	95	99	96
	60	12	99	99	98
Ally	3	0	35	69	25
Cpd. P + Ally	15 + 3	4	98	99	97

(a) Rate of application is in grams of active ingredient/hectare (g/ha).

(b) Represents days after treatment.

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Table VI

Percent Weed Control and Percent Wheat Discoloration by Compound P Alone and in Combination with Ally® Herbicide in Spring Wheat Evaluated 7 and 21 Days After Treatment

Herbicide	Rate lb/a ^(a)	PD(b) in Spring Wheat	Redroot Pigweed	Common Lambs- quarters	Tansy- mustard	Kochia	Wild Buck- wheat	Russian Thistle
Percent Control								
		7	21	21	21	21	21	21
Cpd. P	0.015	2	43	45	95	23	43	25
	0.031	4	63	80	100	45	50	43
Ally	0.002	0	90	10	100	10	65	30
Cpd. P + Ally	0.015 + 0.002	3	90	55	100	33	40	50
	0.031 + 0.002	3	84	75	100	38	80	53

(a) Rate of application is in pounds of active ingredient/acre (lb/a).

(b) PD is percent discoloration in wheat.

Table VII
Percent Weed Control by Compound P Alone and in Combination with Ally® Herbicide in Spring Wheat
Evaluated 30 Days After Treatment

Herbicide	Rate lb/a(a)	Percent Control										
		Redroot Pigweed	Common Ragweed	Wild Sunflower	Common Marsh- elder	Kochia	Wild Buck- wheat	Pennsyl- vania Smart- weed	Russian Thistle	Wild Must- ard	Velvet- leaf	Common Lambs- quarters
Cpd. P	0.031	87	0	92	98	89	40	10	86	54	95	97
	0.063	96	3	95	98	96	75	13	95	60	99	100
Cpd. P + Ally	0.031 + 0.002	92	13	97	98	91	33	99	89	98	-----	-----

(a) Rate of application is in pounds of active ingredient /acre (lb/a).

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Tables VIII and IX (below) demonstrate the improved effect obtained in controlling weeds in post-emergence spring and winter wheat by combining 2,4-dichlorophenoxy acetic acid ethyl ester ("2,4-D ester") with Compound P, as compared with the effect of either component alone.

In Tables VIII and IX the expected synergistic effect was calculated as follows, using the Compound P observed values at 0.031 lb./a, and the 2,4-D observed values at 0.50 lb./a:

$$\text{Expected} = \text{Cmpd P (obs.)} + \frac{2,4\text{-D (obs.)}(100 - \text{Cmpd P (obs.)})}{100}$$

100

In these two tables (VIII and IX) the formulations employed comprised for Compound P a 2.0 lb/gal. emulsifiable concentrate; and for the 2,4-D ethyl ester a commercially available emulsifiable concentrate, each diluted to obtain the indicated application rates.

Table VIII
PERCENT CONTROL OF WEEDS IN WINTER WHEAT WITH A CMPD P COMBINATION
WITH 2,4-D ISOOCYL ESTER 15 DAYS AND 30 DAYS AFTER TREATMENT

Plant Species	15 DAYS AFTER TREATMENT			
	CMPD P Applied Alone at 0.031 lb/a	CMPD P Applied Alone at 0.063 lb/a	2,4-D Ethyl Ester Applied Alone at 0.5 lb/a	CMPD P Applied at 0.031 lb/a in Combination with 2,4-D Ethyl Ester Applied at 0.25 lb/a
Common Ragweed	Observed 0*	Observed 1	Observed 67	Observed 99
Shepardspurse	30	95	15	87
Bittercress	35	83	17	90
Sticky Chickweed	17	20	0	25
Common Lambsquarter	59	89	74	100
Blue Mustard	68	81	32	89
Field Bindweed	62	96	15	95
Tansymustard	45	51	58	93
Flixweed	80	94	23	94
Bushy Wallflower	82	96	29	92
Pennsylvania Smartweed	16	39	16	80
Common Groundsel	40	49	9	73
Common Chickweed	5	12	5	50
Field Pennycress	94	96	94	98
Velvetleaf	99	100	97	100

Table VIII continued

Plant Species	CMPD P Applied Alone at 0.031 lb/a	CMPD P Applied Alone at 0.063 lb/a	2,4-D Ethyl Ester Applied Alone at 0.5 lb/a	CMPD P Applied at 0.031 lb/a in Combination with 2,4-D Ethyl Ester Applied at 0.25 lb/a
30 DAYS AFTER TREATMENT				
Shepardspurse	Observed 93	Observed 98	Observed 20	Observed 97
Bittercress	90	95	77	95
Smallseed Falseflax	57	88	51	86
Blue Mustard	51	64	43	96
Tansymustard	68	63	88	100
Flixweed	79	91	39	99
Bushy Wallflower	90	98	45	97
Field Pennycress	98	99	99	99
Common Groundsel	33	44	11	85
Common Chickweed	10	30	5	30
White Clover	100	95	37	90
Sticky Chickenweed	40	10	5	24
Common Lambsquarter	60	89	93	100
Field Bindweed	33	84	53	83
Pennsylvania Smartweed	25	73	15	92
Velvetleaf	98	99	81	97
Winter Wheat	4	.	1	12
				Expected 94
				98
				79
				72
				96
				87
				95
				100
				40
				15
				100
				43
				97
				69
				36
				100
				5

Table IX

PERCENT CONTROL OF WEEDS IN SPRING WHEAT WITH A CMPD P COMBINATION
WITH 2,4-D ISOOCYTL ESTER 15 DAYS AND 30 DAYS AFTER TREATMENT

Plant Species	15 DAYS AFTER TREATMENT			Observed	Expected
	CMPD P Applied Alone at 0.031 lb/a	CMPD P Applied Alone at 0.063 lb/a	2,4-D Ethyl Ester Applied Alone at 0.5 lb/a		
Redroot Pigweed	82*	95	27	96	87
Common Ragweed	0	1	45	99	45
Wild Sunflower	85	91	88	88	98
Common Marchelder	91	90	79	95	98
Kochia	80	90	47	95	89
Wild Buckwheat	35	85	73	93	83
Pennsylvania Smartweed	9	9	25	62	32
Russian Thistle	73	88	36	94	83
Common Lambsquarter	100	100	98	100	100
Velvetleaf	99	100	96	100	100

Table IX continued

<u>Plant Species</u>	<u>30 DAYS AFTER TREATMENT</u>			
	<u>CMPD P Applied Alone at 0.031 lb/a</u>	<u>CMPD P Applied Alone at 0.063 lb/a</u>	<u>2,4-D Ethyl Ester Applied Alone at 0.5 lb/a</u>	<u>CMPD P Applied at 0.031 lb/a in Combination with 2,4-D Ethyl Ester Applied at 0.25 lb/a</u>
Redroot Pigweed	<u>Observed</u> 87	<u>Observed</u> 96	<u>Observed</u> 60	<u>Observed</u> 96
Common Ragweed	0	3	95	100
Wild Sunflower	92	95	97	92
Common Marchelder	98	98	98	97
Kochia	89	96	71	95
Wild Buckwheat	40	75	71	83
Pennsylvania Smartweed	10	13	24	50
Russian Thistle	86	95	73	96
Common Lambsquarter	97	100	91	99
Wild Mustard	54	60	98	98
Velvetleaf	95	99	78	97
Spring Wheat	2	-	0	10
				<u>Expected</u>
				95
				95
				100
				100
				97
				52
				32
				96
				100
				99
				99
				2

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Table X

Weed Species Used in These Tests

<u>Common Name</u>	<u>Scientific Name</u>
Redroot Pigweed	<i>Amaranthus retroflexus</i>
Giant ragweed	<i>Ambrosia trifida</i>
Common Lambsquarters	<i>Chenopodium album</i>
Wild Sunflower	<i>Helianthus sp</i>
Kochia	<i>Kochia scoparia</i>
Wild Buckwheat	<i>Polygonum convolvulus</i>
Russian Thistle	<i>Salsola kali</i>
Wild Mustard	<i>Brassica kabera</i>
Wild Garlic	<i>Allium vineale</i>
Catchweed Bedstraw	<i>Galium aparine</i>
Red Deadnettle	<i>Lamium purpureum</i>
Wild Chamomile	<i>Matricaria chamomilla</i>
Field Forget-me-not	<i>Myosotis arvensis</i>
Corn Poppy	<i>Papaver rhoeas</i>
Common Chickweed	<i>Stellaria media</i>
Ivyleaf Speedwell	<i>Veronica hederifolia</i>
Persian Speedwell	<i>Veronica persica</i>
Field Violet	<i>Viola arvensis</i>
Pineappleweed	<i>Matricaria matricarioides</i>
Mouseearcress	<i>Arabidopsis thaliana</i>
Blackgrass	<i>Alopecurus myosuroides</i>
Prostrate Knotweed	<i>Polygonum aviculare</i>
Cutleaf Cranesbill	<i>Geranium dissectum</i>
White Mustard	<i>Brassica hirta</i>
Tansymustard	<i>Descurainia pinnata</i>
Deadnettle	<i>Lamium sp</i>
Ryegrasses	<i>Lolium sp.</i>
Common ragweed	<i>Ambrosia artemisiifolia</i>
Common marshelder	<i>Iva xanthiifolia</i>
Pennsylvania smartweed	<i>Polygonum pennsylvanicum</i>
Velvetleaf	<i>Abutilon theophrasti</i>

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From the above results in Tables I - IX it will be seen that generally, the combinations of Compound P with the herbicides disclosed herein do provide a broader spectrum of weed control than do each of the herbicides when tested alone. A brief discussion of the tables of data follows:

In Table I, the combination of Compound P and Express herbicide provides greater control of wild buckwheat than either Compound P or Express herbicide when applied alone. The combination of Compound P and Harmony herbicide broadens the spectrum of activity of Compound P to include improved control of giant ragweed, wild sunflower, wild buckwheat, wild mustard, and wild garlic.

In Table II, the combination of Compound P and Express herbicide provides greater control of corn poppy in winter wheat and winter barley than does Compound P alone. In addition, the combination of Compound P and Express herbicide provides greater control of persian speedwell and field violet than either compound when applied alone.

In Table III, the combination of Compound P and Ally herbicide provides greater control of pineappleweed, field violet, and mouseearcress than either Compound P or Ally herbicide alone.

In Table IV, the combination of Compound P and Ally herbicide appears to be particularly efficacious. The combination provides greater control of nearly all of the weed species (i.e. field violet, persian speedwell, common chickweed, field forget-me-not, cutleaf cranesbill, red deadnettle, and ivyleaf speedwell) than does either Compound P or Ally herbicide alone. The

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combination of Compound P and Ally herbicide provides greater than 75% control of all of the weed species in these trials.

- 5 In Table V, the combination of Compound P and Ally herbicide provides nearly 100% control of persian speedwell and white mustard up to about 65 days.

Also, in Table V, the data shows that the combination of
10 Compound P and Ally herbicide is essentially not phytotoxic to wheat.

In Table VI, the combination of Compound P and Ally herbicide broadens the spectrum of activity of both
15 compounds as compared to each when applied alone. The combination, again is essentially not phytotoxic to spring wheat.

In Table VII, the combination of Compound P and Ally
20 herbicide greatly increases the control of Pennsylvania smartweed and wild mustard as compared to the control shown by Compound P when applied alone.

In Tables VIII and IX, Compound P and the 2,4-D ester
25 were tested alone and in combination. The combinations provided a clear showing of synergism as evidenced by the comparison of the observed control from the combination with the expected (calculated) control, shown in the last two columns of Tables VIII and IX.

30 Note especially the results for:

common ragweed, shepherdspurse, bittercress, field bindweed, tansymustard, flixweed, Pennsylvania smartweed, and common groundsel, at 15 days after treatment in Table VIII;

35 for blue mustard, flixweed, common groundsel, field bindweed, and Pennsylvania smartweed, at 30 days after

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treatment in Table VIII;

for redroot pigweed, common ragweed, wild buckwheat, Pennsylvania smartweed, and russian thistle, at 15 days after treatment in Table IX; and

5 for wild buckwheat, at 30 days after treatment in Table IX.

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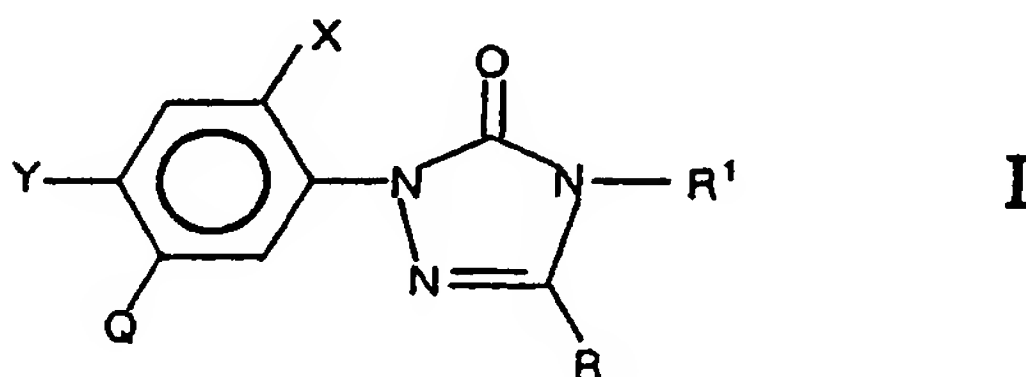
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Claims:

1. An herbicidal composition characterized by a herbicidally effective amount of the combination of:
 (1) a triazolinone of the formula

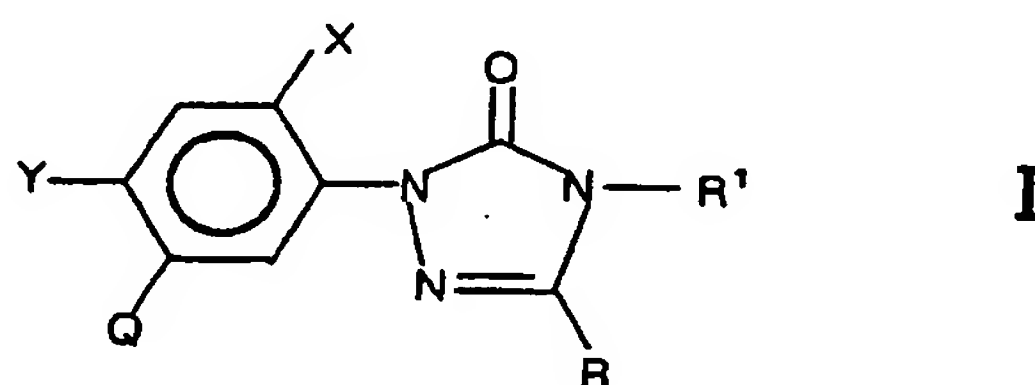


- 5 in which
 R is halogen or lower alkyl;
 R¹ is haloalkyl;
 X is hydrogen, halogen, alkyl, haloalkyl, alkoxy, or
 nitro;
 10 Y is hydrogen, halogen, alkyl, haloalkyl, alkoxy,
 haloalkyl, halo lower alkylsulfinyl, or halo lower
 alkoxy;
 Q is -CH(R²)C(R³)(R⁴)Q' or -CH=C(R⁴)Q';
 R² is H or halogen;
 15 R³ is halogen;
 R⁴ is H or lower alkyl;
 Q' is CO₂H, CO₂R⁵, CON(R⁶)(R⁷), CN, CHO, or C(O)R⁵;
 R⁵ is alkyl, alkoxycarbonylalkyl, cycloalkyl,
 benzyl, chlorobenzyl, alkylbenzyl, or haloalkylbenzyl;
 20 and each of R⁶ and R⁷ is independently H, or a radical
 which is an alkyl, cycloalkyl, alkenyl, alkynyl, alkoxy,
 phenyl, benzyl or SO₂R₆ (in which R₆ is other than H) or
 is one of said radicals substituted by halogen, alkyl,
 or cyano;
 25 or a base-addition salt of the compound in which Q'
 is CO₂H; with the proviso that any alkyl, alkenyl, or
 alkynyl moiety have less than 6 carbon atoms and that
 any cycloalkyl moiety have 3 to 7 carbon atoms, and
 (2) dichloro- or chloro-lower alkylphenoxy lower

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alkanoic acids, or their corresponding herbicidally effective esters, or alkali metal or ammonium salts, in admixture with a suitable carrier.

2. An herbicidal composition characterized by a
 5 herbicidally effective amount of the combination of:
 (1) a triazolinone of the formula

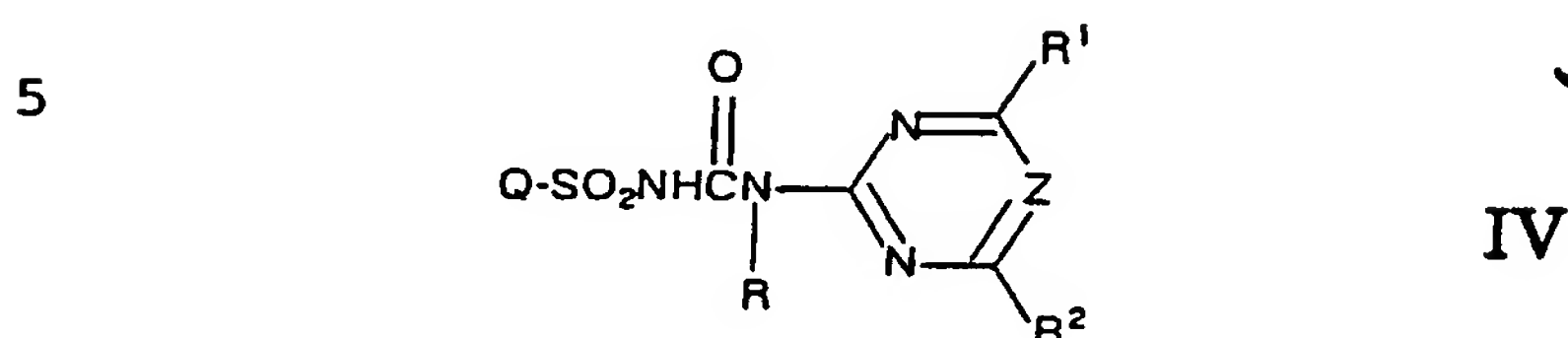


in which

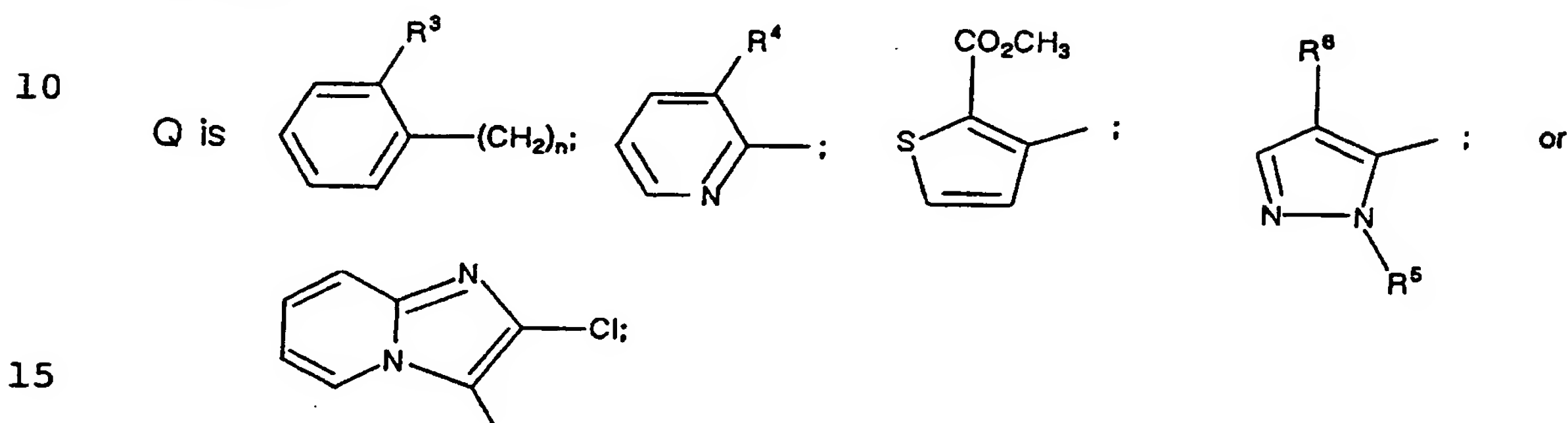
- R is halogen or lower alkyl;
 R¹ is haloalkyl;
 10 X is hydrogen, halogen, alkyl, haloalkyl, alkoxy, or
 nitro;
 Y is hydrogen, halogen, alkyl, haloalkyl, alkoxy,
 haloalkyl, halo lower alkylsulfinyl, or halo lower
 alkoxy;
 Q is -CH(R²)C(R³)(R⁴)Q' or -CH=C(R⁴)Q';
 15 R² is H or halogen;
 R³ is halogen;
 R⁴ is H or lower alkyl;
 Q' is CO₂H, CO₂R⁵, CON(R⁶)(R⁷), CN, CHO, or C(O)R⁵;
 R⁵ is alkyl, alkoxycarbonylalkyl, cycloalkyl,
 20 benzyl, chlorobenzyl, alkylbenzyl, or haloalkylbenzyl;
 and each of R⁶ and R⁷ is independently H, or a radical
 which is an alkyl, cycloalkyl, alkenyl, alkynyl, alkoxy,
 phenyl, benzyl or SO₂R₆ (in which R₆ is other than H) or
 is one of said radicals substituted by halogen, alkyl,
 25 or cyano;
 or a base-addition salt of the compound in which Q'
 is CO₂H; with the proviso that any alkyl, alkenyl, or
 alkynyl moiety have less than 6 carbon atoms and that

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any cycloalkyl moiety have 3 to 7 carbon atoms, and
 (2) a sulfonylurea of the formula



wherein



Z is N or CH;

R is H or -CH₃;

R¹ and R² are -OCH₃ or -CH₃;

R³ is CO₂CH₃ or Cl;

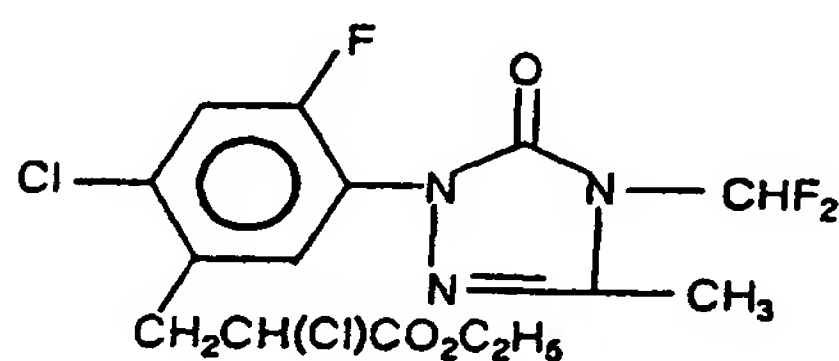
20 n is 0 or 1;

R⁴ is CN(CH₃)₂ or SO₂C₂H₅;

25 R⁵ is CH₃ or ; and

R⁶ is CR⁷, wherein R⁷ is -OCH₃ or -OC₂H₅.

3. The composition of claim 1 characterized by a
 30 triazolinone of the formula



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and a dichloro- or chloro-lower alkylphenoxy lower alkanolic acid or its corresponding herbicidally effective ester, or alkali metal or ammonium salts in admixture with a suitable carrier.

5 4. The composition of claim 3 characterized in that the phenoxy alkanolic acid is 2,4-D.

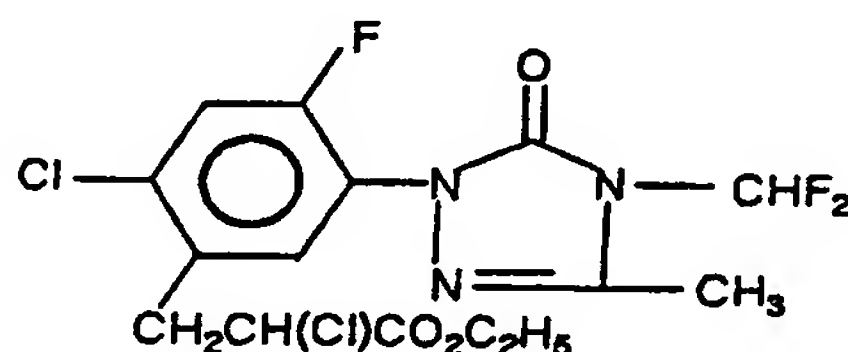
5. The composition of claim 3 characterized in that the phenoxy alkanolic acid is 2,4-D ammonium salt.

10 6. The composition of claim 3 characterized in that the phenoxy alkanolic acid is MCPA ammonium salt.

7. The composition of claim 3 characterized in that the phenoxy alkanolic acid is MCPPP.

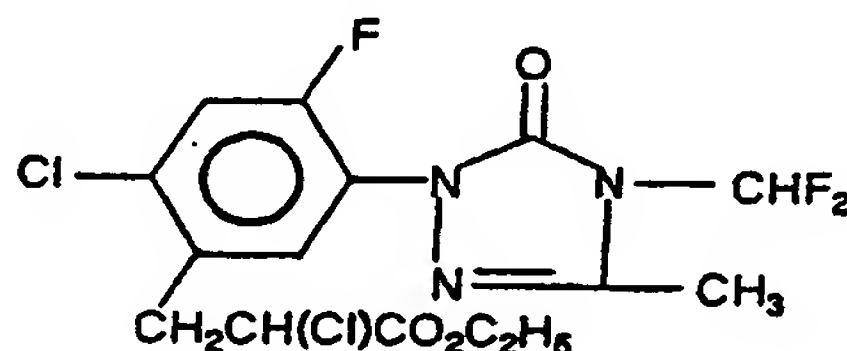
8. The composition of claim 2 characterized in that the triazolinone is

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20 and the sulfonylurea is metsulfuron-methyl, in admixture with a suitable carrier.

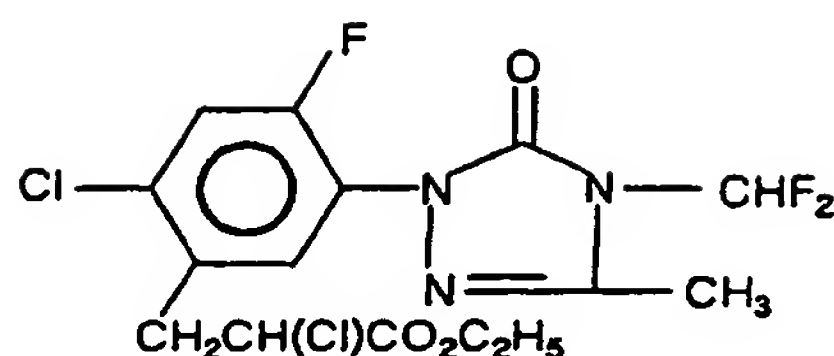
9. The composition of claim 2 characterized in that the triazolinone is



25 and the sulfonylurea is chlorosulfuron, in admixture with a suitable carrier.

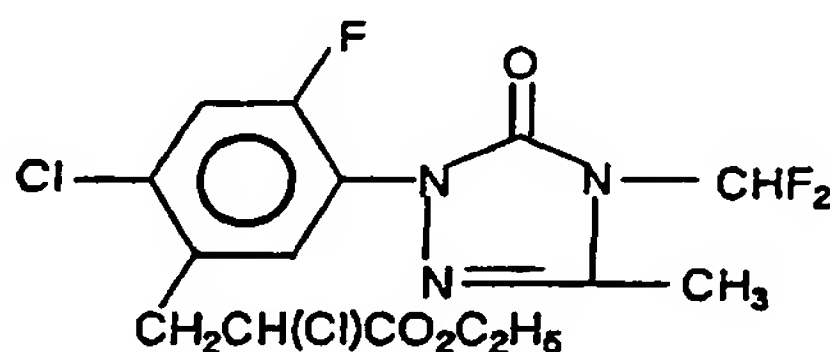
10. The composition of claim 2 characterized in that the triazolinone is

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and the sulfonylurea is tribenuronmethyl, in admixture with a suitable carrier.

11. The composition of claim 2 characterized in that the triazolinone is



5 and the sulfonylurea is thifensulfuronmethyl, in admixture with a suitable carrier.

12. A method for controlling undesired plant growth characterized by applying to the locus where control is desired a herbicidally effective amount of the composition of claim 1.

13. A method for controlling undesired plant growth characterized by applying to the locus where control is desired a herbicidally effective amount of the composition of claim 2.

14. A method for controlling undesired plant growth characterized by applying to the locus where control is desired a herbicidally effective amount of the composition of claim 3.

15. A method for controlling undesired plant growth characterized by applying to the locus where control is desired a herbicidally effective amount of the composition of claim 4.

16. A method for controlling undesired plant growth characterized by applying to the locus where control is

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desired a herbicidally effective amount of the composition of claim 5.

17. A method for controlling undesired plant growth characterized by applying to the locus where control is
5 desired a herbicidally effective amount of the composition of claim 6.

18. A method for controlling undesired plant growth characterized by applying to the locus where control is
10 desired a herbicidally effective amount of the composition of claim 7.

19. A method for controlling undesired plant growth characterized by applying to the locus where control is
desired a herbicidally effective amount of the composition of claim 8.

15 20. A method for controlling undesired plant growth characterized by applying to the locus where control is desired a herbicidally effective amount of the composition of claim 9.

21. A method for controlling undesired plant growth
20 characterized by applying to the locus where control is desired a herbicidally effective amount of the composition of claim 10.

22. A method for controlling undesired plant growth
25 characterized by applying to the locus where control is desired a herbicidally effective amount of the composition of claim 11.

30

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/10057**A. CLASSIFICATION OF SUBJECT MATTER**IPC(5) : A01N 39/02, 39/04, 43/10, 43/40, 43/52, 43/54, 43/56, 43/653
US CL : 504/134, 135, 139, 145

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 504/134, 135, 139, 145, 211, 212, 213, 214, 215, 273, 323

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO, A, 90/02120 (POSS ET AL) 03 September 1990, see entire document.	1-22
Y	US, A, 4,127,405 (LEVITT ET AL) 28 November 1978, see entire document.	2, 9, 13, 20
Y	US, A, 4,481,029 (LEVITT) 06 November 1984, see entire document.	2, 11, 13, 22
Y	US, A, 4,238,621 (LEVITT) 09 December 1980, see entire document.	2, 8, 10, 13, 19, 21
Y	US, A, 4,370,480 (LEVITT ET AL) 25 January 1983, see entire document.	2

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Z" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

30 December 1993

Date of mailing of the international search report

13 JAN 1994

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
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Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/10057

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 2,471,575 (MANSKE) 31 May 1949, see entire document.	1, 3-5, 12, 14-16
Y	US, A, 2,740,810 (SKEETERS) 03 April 1956, see entire document.	1, 3, 6, 7, 12, 14, 17, 18
A	US, A, 4,318,731 (KAJIOKA ET AL) 09 March 1982.	1-22
A	US, A, 4,398,943 (KAJIOKA ET AL) 16 August 1983.	1-22
A	US, A, 4,818,276 (MARAVETZ ET AL) 04 April 1989.	1-22
A	US, A, 4,919,708 (MARAVETZ) 24 April 1990.	1-22
Y,P, &	US, A, 5,217,520 (POSS) 08 June 1993.	1-22
Y,&	US, A, 5,125,958 (POSS) 30 June 1992.	1-22

Form PCT/ISA/210 (continuation of second sheet)(July 1992)★

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/10057

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
(Form PCT/ISA/206 Previously Mailed.)
Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐

The additional search fees were accompanied by the applicant's protest.

☒

No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/10057

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

- I. Claims 1, 3-7, 12 and 14-18, drawn to a herbicidal composition and method of use of the triazolinone of formula I in combination with a dichloro- or chloro loweralkylphenoxy loweralkanoic acid ester or salt; Class 504, subclass 139.
- II. Claims 2, 8-10, 13 and 19-21, drawn to a herbicidal composition and method of use of the triazolinone of formula I in combination with a sulfonyl urea of formula IV wherein Q is a substituted phenyl or benzyl group; Class 504, subclass 135.
- III. Claim 2, drawn to a herbicidal composition and method of use of a triazolinone of formula I in combination with a sulfonylurea of formula IV wherein Q is a substituted pyridyl group; Class 504, subclass 134.
- IV. Claims 2, 11, and 22, drawn to a herbicidal composition and method of use of a triazolinone of formula I in combination with a sulfonylurea of formula IV wherein Q is a substituted thiophene group; Class 504, subclass 135.
- V. Claim 2, drawn to a herbicidal composition and method of use of a triazolinone of formula I in combination with a sulfonylurea of formula IV wherein Q is a disubstituted pyrazole group; Class 504, subclass 135.
- VI. Claim 2, drawn to a herbicidal composition and method of use of a triazolinone of formula I in combination with a sulfonylurea of formula IV wherein Q is a imidazopyridine group; Class 504, subclass 135.

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